Samples of the 50:50 mixtures of D1-Cl and D2-Cl were purified as colorless liquids by preparative GLC for characterization:[16] ^{1}H NMR (neat, D_2O lock) δ –0.20 (br s, 12 H), 0.42 (m, 1 H), 0.52 (s, 9 H), 1.26 (m, 2 H), 6.96–7.02 (br m, 5 H); MS, m/z (relative intensity) 297 (12, P – 15), 298 (4), 299 (5), 300 (1), 147 (100), 141 (10), 121 (16), 73 (31), 45 (15). Anal. Calcd for $C_{16}H_{29}Si_2Cl$: C, 61.39; H, 9.34. Found: C, 61.14; H, 9.37.

Free Radical Chlorination of D1-H and D2-H. To a solution of 1.0 mL (3.5 mmol) of a 38:62 mixture of D1-H and D2-H in 25 mL of carbon tetrachloride was added 6.8 mg of benzoyl peroxide, and the resulting solution was refluxed for 12 h. GLC analysis of the reaction mixture indicated the formation of a 38:62 mixture of D1-Cl and D2-Cl in 90% yield. When the same reaction was carried out by using a 5:95 mixture of D1-H and D2-H, there was obtained a 93% yield of a 5:95 mixture of D1-Cl and D2-Cl.

Methanolysis of D1-Cl and D2-Cl. To a solution of 1 mL of dry methanol and 2 mL of cyclohexylamine in 30 mL of pentane cooled to 0 °C was added dropwise a solution of 0.92 g (2.9 mmol) of a 38:62 mixture of D1-Cl and D2-Cl in 15 mL of pentane. The reaction mixture was stirred for 4 h after the formation of the amine hydrochloride precipitate was observed. After hydrolytic workup and solvent evaporation under reduced pressure GLC analysis showed a 90% yield of a 62:38 mixture of D1-OMe and D2-OMe. A similar experiment using a 5:95 mixture of D1-Cl and D2-Cl gave a 93:7 mixture of D1-OMe and D2-OMe in 88% yield.

2-Fluoro-2-phenyl-5,5-dimethyl-3-(trimethylsilyl)-2-silahexane, D1- and D2-F. To a solution of 0.43 mL (3.5 mmol) of boron trifluoride etherate in 5 mL of ether was added 1.0 mL (3.5 mmol) of a 35:65 mixture of D1-OMe and D2-OMe. After the mixture was stirred for 12 h, GLC analysis of the mixture showed the formation of a 66:34 mixture of D1-F and D2-F in 90% yield. A similar reaction starting with a 5:95 mixture of D1-OMe and D2-OMe gave a 91% yield of a 93:7 mixture of D1-F and D2-F. Pure mixtures of the diastereomers were isolated by preparative GLC for characterization as colorless liquids: ^{1}H NMR (neat, D_2O lock) δ –0.30 (s, 9 H), 0.28 (d, J_{H-F} = 2.86 Hz, 3 H), 0.13 (m, 1 H), 0.49 (s, 9 H), 1.26 (m, 2 H), 6.89–7.20 (br, 5 H); MS, m/z (relative intensity) 281 (9, P – 15), 204 (13), 147 (100), 141 (14), 121 (19), 73 (39), 59 (10), 45 (12). Anal. Calcd for $C_{16}H_{29}Si_2F$: C, 64.80; H, 9.86. Found: C, 64.94; H, 9.84.

Lithium Aluminum Hydride Reduction of D1- and D2-F to D1- and D2-H. To a stirred mixture of 50 mg (1.4 mmol) of lithium aluminum hydride in 3 mL of ether was added 0.90 g (3.0 mmol) of a 66:34 mixture of D1-F and D2-F. After the mixture was stirred at room temperature for 12 h, GLC analysis showed the formation of a 90% yield of a 30:70 mixture of D1-H and D2-H. When the reduction was carried out by using a 93:7 mixture of D1-F and D2-F, there was obtained an 8:92 mixture of D1-H and D2-H in 91% yield.

Acknowledgment. This work was supported by the National Science Foundation, Grant CHE 8100668, the Robert A. Welch Foundation, and the North Texas State Faculty Research Fund.

Registry No. (*E*)-**2**, 85803-40-3; (*Z*)-**2**, 85803-41-4; **3**, 94597-07-6; D1-OMe, 94597-05-4; D1-H, 94597-08-7; D1-Cl, 94597-10-1; D1-F, 94597-12-3; D2-OMe, 94597-06-5; D2-H, 94597-09-8; D2-Cl, 94597-11-2; D2-F, 94597-13-4; *t*-BuLi, 594-19-4; Me_3SiOMe, 1825-61-2; PhCOCl, 98-88-4; PCl_3, 7719-12-2; $SOCl_2$, 7719-09-7; CCl_4, 56-23-5; $(PhCO_2)_2$, 94-36-0; vinylphenylmethylchlorosilane, 17306-05-7; anthracene, 120-12-7.

Silabenzene and Silafulvene by Ring Contraction and Expansion of Cyclic Silylcarbenes

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Received July 24, 1984

Thermolysis of diazo-2,2-dimethyl-3,4,5,6-tetraphenyl-2-silacyclohexa-3,5-diene resulted in the formation of 1,2,3,4-tetraphenyl-6,6-dimethyl-6-silafulvene by the ring contraction of 2,2-dimethyl-3,4,5,6-tetraphenyl-2-silacyclohexa-3,5-dienylidene. Silacyclopentadienylmethylene generated from thermolysis and photolysis of (1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)diazomethane and (1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)diazirine rearranged to 2,3,4,5-tetraphenyl-1-silatoluene by the ring expansion and to 1,2,3,4-tetraphenyl-6-methyl-5-silafulvene by 1,2 migration of a methyl group. These sp^2-hybridized silicon species were successfully trapped by alcohols, ketone, and diene. However, photolysis of 1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)diazoethane gave normal carbene products. The reactions of cyclic silyl diazo compounds diazo-2,2-diphenyl-4-bromo-1,2-dihydro-2-silanaphthalene and 10-diazo-9,9-dimethyl-9,10-dihydro-9-silaanthracene are also described.

Introduction

In recent years, interest in the chemistry of α-silylcarbenes has remarkably increased,[1] and detailed studies of α-silylcarbenes; silylcarboalkoxycarbenes,[2] silylketocarbenes,[3] silylphenylcarbenes,[4] (trimethylsilyl)carbene,[5] disilylcarbenes,[6] and their derivatives have been reported.

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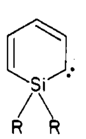
The proposed intramolecular reaction of α-silylcarbenes to produce reactive sp^2-hybridized silicons (silenes) has attracted interest in particular. However, the silylcarbenes investigated so far have been linear and simply substituted ones, and no systematic study of cyclic silylcarbenes has been reported.[7] Cyclic silylcarbenes **1**–**3** are particularly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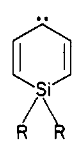
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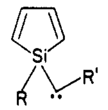
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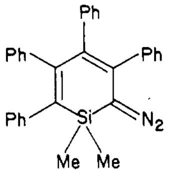
interesting because they are expected to produce silabenzene by the rearrangement of a substituent on silicon atom to a carbene center (1,2 and 1,4 migration of R for **1** and **2**, respectively, and ring expansion for **3**). Silafulvenes would also be expected by ring contraction for **1** and 1,2 migration of R for **3**. It is well precedented that the analogous all-carbon carbenes give benzene derivatives by the intramolecular reaction,[8] and one could quite reasonably anticipate cyclic silylcarbenes to behave similarly. We report here the detailed study of the cyclic silylcarbenes derived from cyclic silyl diazo compounds: diazo-2,2-dimethyl-3,4,5,6-tetraphenyl-2-silacyclohexa-3,5-diene (**4**), diazo-2,2-diphenyl-4-bromo-1,2-dihydro-2-silanaphthalene (**5**), 10-diazo-9,9-dimethyl-9,10-dihydro-9-silaanthracene (**6**), (1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)diazomethane (**7**), and (1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)diazoethane (**8**).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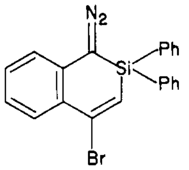
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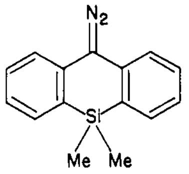
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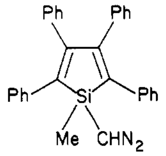
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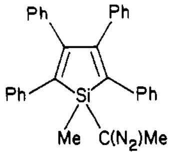
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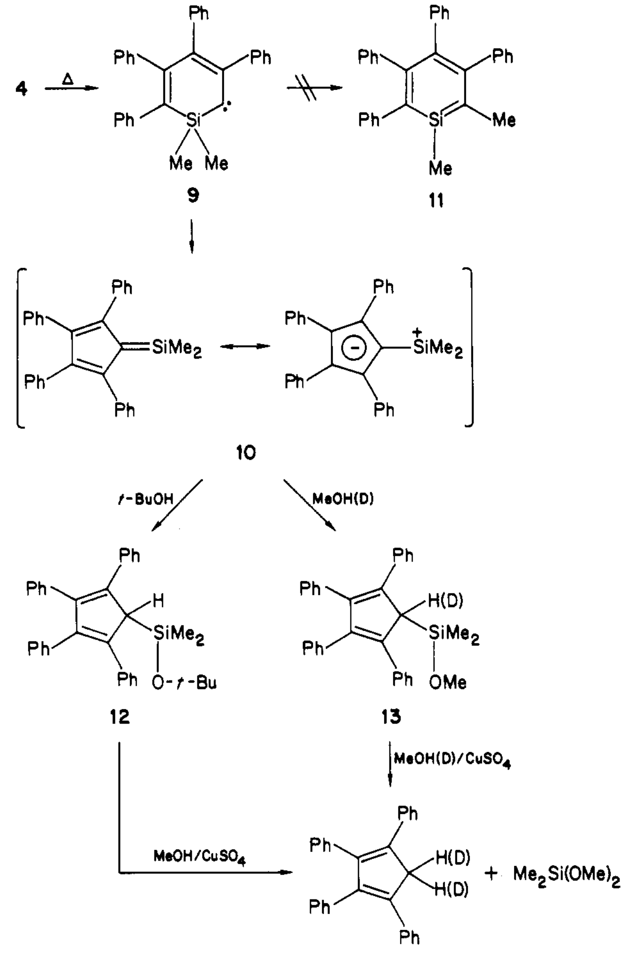
Scheme I



Both silabenzene[9] and silafulvene[10] are attractive molecules due to the aromaticity of sp^2-hybridized silicon and to the enhanced stability of silafulvenes. They have been generated by the thermally induced retroene route, β-elimination of methoxysilane or lithium chloride. Silabenzenes were spectroscopically confirmed by the matrix method at low temperature.[11] Since the notorious instability of silenes makes it unlikely that silabenzene or silafulvene would be stable under normal conditions, it was decided to take advantage of the rapid reaction of silenes with alcohols, carbonyl compounds, and dienes in the hope of isolating trapped products.

Results and Discussion

Reactions of Diazo-2,2-dimethyl-3,4,5,6-tetraphenyl-2-silacyclohexa-3,5-diene (4) and Diazo-2,2-diphenyl-4-bromo-1,2-dihydro-2-silanaphthalene (5). When a benzene solution of **4** containing an excess of *tert*-butyl alcohol was heated in a sealed tube at ca. 100 °C in the presence of a catalytic amount of anhydrous cupric sulfate, a vigorous reaction occurred with evolution of nitrogen and ceased in a few minutes. Separation of the reaction mixture by silica gel chromatography gave (1,2,3,4-tetraphenylcyclopentadiene-5-yl)dimethyl-*tert*-butoxysilane (**12**) in 96% yield as white crystals. The

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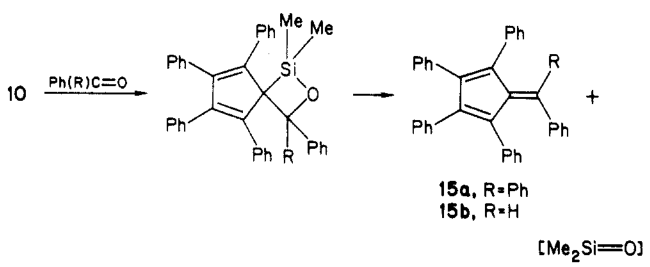
Scheme II



characteristic upfield shift of the silyl methyl groups (−0.23 ppm in CCl_4) was observed by the shielding effects of the two phenyl rings at 1- and 4-positions. The *tert*-butoxysilane **12** was also obtained in 84% yield when **4** was reacted with *tert*-butyl alcohol at 130 °C in the absence of cupric sulfate, but the reaction was very slow (1 h).

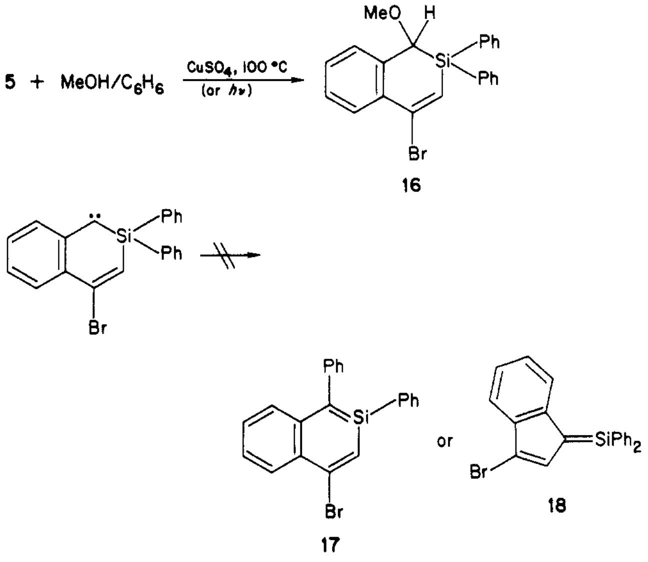
The formation of **12** provides strong evidence for the formation of 1,2,3,4-tetraphenyl-6,6-dimethyl-6-silafulvene (**10**) by the migration of a dienyl group to a carbene center (Scheme I). No product from 2,3,4,5-tetraphenyl-6-methyl-1-silatoluene (**11**), which would be formed by the methyl migration, was found. It seems reasonable that the dipolar form of the silafulvene **10** would have enhanced importance because of the stability of the cyclopentadienyl anion.

The evidence for the silafulvene **10** was further substantiated by similar reactions with methanol and methanol-d_1. The reaction of **4** with methanol gave 1,2,3,4-tetraphenyl-1,3-cyclopentadiene (**14**) in 91% yield, probably formed by methanolysis of methoxysilane **13**. Indeed, *tert*-butoxysilane **12** was found to give the desilylated cyclopentadiene **14** in 96% yield under the reaction conditions. The reaction of **4** with methanol-d_1 led to the formation of 1,2,3,4-tetraphenyl-5,5-dideuterio-1,3-cyclopentadiene in 95% yield. The peak at δ 3.97 in the NMR spectrum, attributed to the methylene protons of the cyclopentadiene, was absent. The mass spectrum (*m/e* 372 (M^+)) also showed the incorporation of the two deuterium atoms.

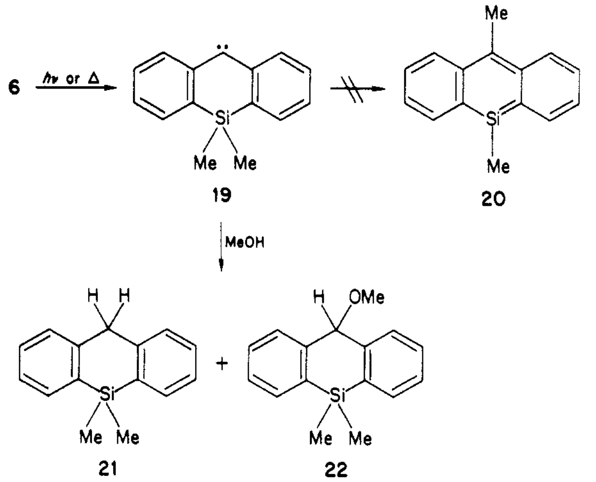
Further support for the intervention of **10** was obtained by the reaction of **4** with carbonyl compounds. A benzene solution of **4** containing an excess of benzophenone was subjected to thermolysis at ca. 100 °C in the presence of cupric sulfate to afford 1,2,3,4,6,6-hexaphenylfulvene (**15a**) in 66% yield as almost black crystals. The fulvene **15a** was also obtained in 49% yield in the absence of the catalyst (Scheme II). However, the fulvene was not formed in the reaction of 1,2,3,4-tetraphenyl-1,3-cyclopentadiene with benzophenone under the same reaction conditions. Since it is well documented that silenes are intercepted by carbonyls to produce olefins and silanones via pseudo Wittig-type reactions, the fulvene **15a** might be formed by the reaction of **10** with benzophenone.[12] The reaction of **4** with benzaldehyde in the presence of cupric sulfate produced 1,2,3,4,6-pentaphenylfulvene (**15b**) in 44% yield as rust-red crystals. These results show that the reaction of **4** occurred only in the direction to form 6-silafulvene (**10**).

The reaction of diazosilanaphthalene **5** was quite different from that of **4**. Thermolysis of **5** in benzene/methanol solution at 100 °C for 5 min in the presence of cupric sulfate gave a simple O–H insertion product **16** in 96% yield. Photolysis of **5** in methanol also produced **16** in 74% yield. Products derived from silanaphthalene **17** nor benzosilafulvene **18** were absent (Scheme III).

Scheme III



Scheme IV



Reaction of 10-Diazo-9,9-dimethyl-9,10-dihydro-9-silaanthracene (6). Although 1,4 migration of a substituent to a carbene center is not so familiar, it has been known that the gas-phase pyrolysis of 4,4-dimethyldiazocyclohexadiene affords *p*-xylene and toluene.[8a] However, an analogous reaction of 4,4-dimethyl-4-silacyclohexadienylidene did not give silabenzenes.[13] We also expected the formation of silaanthracene **20** from dibenzosilacyclohexadienylidene **19** (silaanthracenylidene) via 1,4 methyl migration. Reaction of **6** was performed in the gas phase at ca. 500 °C in a vertical flow pyrolysis apparatus. The methanol/benzene solution of **6** was introduced by syringe through a septum with a nitrogen stream into the heated Pyrex tube. The pyrolysis produced a complex product mixture of which the identifiable products were **21** (15%) and **22** (10%), and a considerable quantity of unidentified materials was formed. Photolysis of **6** in methanol produced **22** in 95% yield. No evidence for the intermediacy of silanaphthalene **20** was observed (Scheme IV).

Reactions of (1-Methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)diazomethane (7) and (1-Methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)diazoethane (8). Ring expansion of silacyclopentadienylcarbene **3** is expected to provide convenient access to silabenzene.

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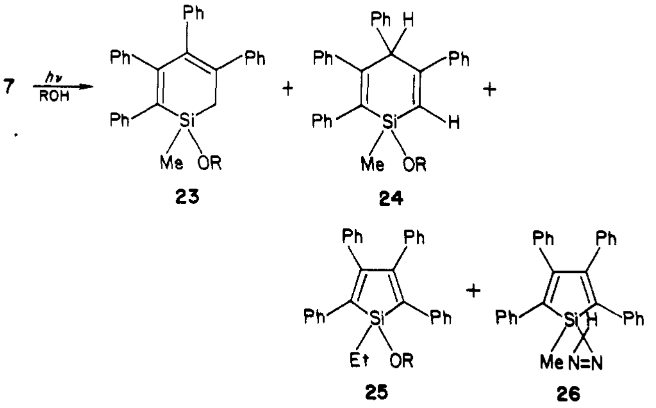
Scheme V



Methylcyclopentadienylcarbene is known to produce toluene together with 1-methylbenzvalene and spiro[4.2]-heptadiene by ring expansion, 1,4 carbene addition, and C–H insertion, respectively.[8b,c] Arsabenzenes are also accessible by similar ring expansions.[14] Photolysis of a benzene solution of **7** in an excess of methanol gave 1-methyl-1-methoxy-2,3,4,5-tetraphenyl-1-silacyclohexa-2,4-diene (**23**) (7%, R = Me), 1-methyl-1-methoxy-2,3,4,5-tetraphenyl-1-silacyclohexa-2,5-diene (**24**) (8%, R = Me), 1-ethyl-1-methoxy-2,3,4,5-tetraphenyl-1-silacyclopentadiene (**25**) (19%, R = Me), and (1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)diazirine (**26**) (48%) (Scheme V).[15] Photolysis in methanol-d_1 afforded similar products, and deuterium was incorporated into each of the products.

The products **23** and **24** apparently are derived from 1,2 and 1,4 addition of methanol to 2,3,4,5-tetraphenyl-1-silatoluene (**28**) which arises by the ring expansion of (1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)-methylene **27**. Compound **25** is a product derived from 1,2,3,4-tetraphenyl-6-methyl-5-silafulvene (**29**) formed by the methyl shift to the carbene center (Scheme VI). Similarly, in *tert*-butyl alcohol, 1-methyl-1-*tert*-butoxy-2,3,4,5-tetraphenyl-1-silacyclohexa-2,4-diene (**23**), (14%, R = *t*-Bu), 1-ethyl-1-*tert*-butoxy-2,3,4,5-tetraphenyl-1-silacyclopentadiene (**25**) (15%, R = *t*-Bu), and the diazirine **26** (38%) were produced. It is of interest to note that the 1,4 addition product of *tert*-butyl alcohol to **28** was not found. Since methanol adds to conjugated silenes in a stepwise manner, 1,2 and 1,4 addition occurs.[16] By contrast, a concerted process might be involved in *tert*-butyl alcohol.

Diazirine **26** was relatively stable toward the light of a wavelength greater than 350 nm. Thus, a benzene solution of **7** was irradiated with filtered light (>350 nm) to give **26** as greenish yellow crystals in 64% yield. Diazirine itself also was found to produce the carbene **27** under these photochemical conditions. Photolysis of **26** in *tert*-butyl alcohol without the filter solution gave **23** (13%, R = *t*-Bu), **25** (19%, R = *t*-Bu), and 32% of unreacted **26**. Photochemical reactions of **7** and **26** under the various conditions are summarized in Table I. The results reveal the unique migrating tendency of the groups on silicon atom. Product ratio (**23** + **24**/**25**) of silabenzene **28** and silafulvene **29** did not vary significantly, indicating that the migrating ability of the methyl group is almost two times greater than that of the vinyl group on the basis of a statistical factor.

Table I. Photolysis of 7 and 26 in Alcohols

substrate	irr time, h	solv	product, % 23	24	25	26	ratio 23 + 24/25
7	6	MeOH/C_6H_6	7	8	19	48	0.8
7	18	MeOD/C_6H_6	3	27	37	9	0.8
7	6	*t*-BuOH/C_6H_6	14	0	15	38	0.9
7[a]	3	MeOH/C_6H_6	8	6	15	54	0.9
7[a]	3	*t*-BuOH/C_6H_6	13	0	13	68	1.0
26	12	*t*-BuOH/C_6H_6	13	0	19	32	0.7

[a] A methanol solution of phenanthrene (10 g/L) was used as a filter solution (path length 1 cm).

We next turned to the thermal decomposition of **7** and **26**. (Silacyclopentadienyl)diazomethane **7** was thermally stable and survived even after being heated in xylene for 1 h, but it readily decomposed in the presence of cupric sulfate to give unidentified polymeric products. In contrast, the diazirine **26** decomposed when heated in the absence of the catalyst, and products **23** (49%, R = *t*-Bu) and **25** (31%, R = *t*-Bu) were obtained in *tert*-butyl alcohol at 150 °C for 15 min. Similarly, in methanol, **23** (22%, R = Me), **24** (22%, R = Me), and **25** (42%, R = Me) were formed.

The silabenzene **28** and silafulvene **29** also were trapped by the diene and the carbonyl, respectively. (Silacyclopentadienyl)diazirine **26** was thermally decomposed in 2,3-dimethyl-1,3-butadiene to give Diels–Alder adduct **30** in 14% yield. 1,1-Diphenylpropene was isolated in 14% yield in the presence of benzophenone (Scheme VII). Although 5-silafulvene **29** has not been reported previously, its reactivity seems to be quite similar to that of known silenes.

It is now clear from these results that silabenzene and 5-silafulvene are involved in the reaction of the silacyclopentadienylcarbene. However, in the case of (silacyclopentadienyl)diazoethane **8** hydrogen migration to give a vinylsilane is preferred over the migration of dienyl or methyl groups. Photolysis of **8** in *tert*-butyl alcohol resulted in the formation of 1-methyl-1-vinyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene **31** (52%) and diazirine **32** (27%). A product from neither silabenzene nor silafulvene was found (Scheme VIII).

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded with either a Varian EM 360A or a JEOL FX-99 spectrometer. IR, mass, and UV spectra were obtained on a Hitachi 260-50 spectrometer, a Hitachi RMU-6M mass spectrometer, and a Shimazu UV-365 spectrometer, respectively. Preparative HPLC was carried out on a LC-08 (Japan Analytical Ind. Co., LTD). Preparative gas chromatographic separations were carried out on an Ohukura gas chromatograph with a 8 mm × 1 m glass column of 10% SF-96 on Celite 545. All melting points were uncorrected.

Materials. Diazo-2,2-dimethyl-3,4,5,6-tetraphenyl-2-silacyclohexa-3,5-diene (**4**), diazo-2,2-diphenyl-4-bromo-1,2-dihydro-2-silanaphthalene (**5**), and 10-diazo-9,9-dimethyl-9,10-dihydro-9-silaanthracene (**6**) were synthesized according to the literarure procedures.[17]

Preparation of (1-Methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)diazomethane (7). A mixture of 1-methyl-1-chloromethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (9.8 g, 21.8 mmol), THF (10 mL), and magnesium (650 mg, 26.7 mmol) was placed in a flask and stirred under nitrogen. When the reaction

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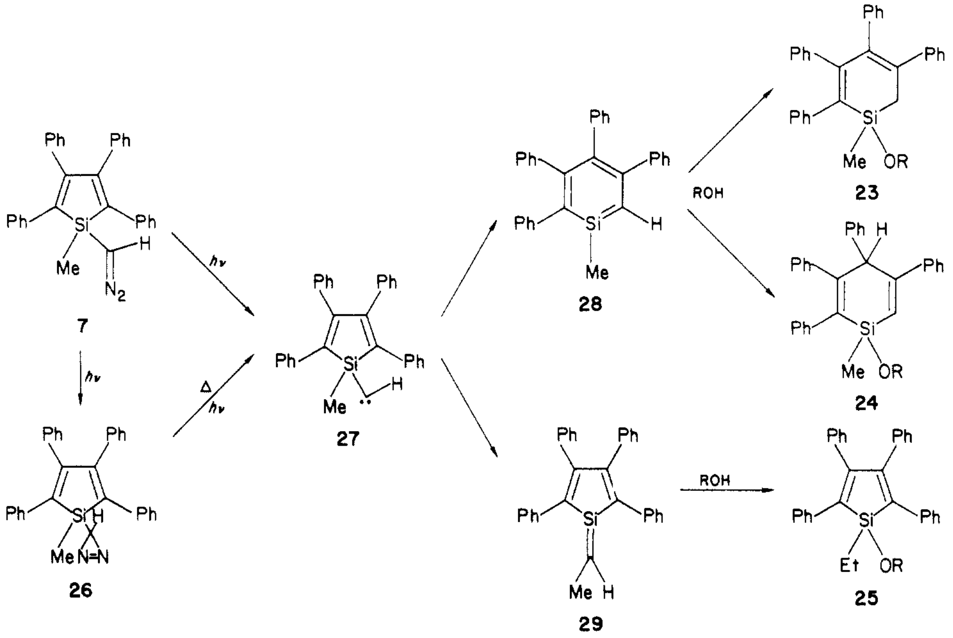
(14) (a) Märkl, G.; Advena, J.; Hauptmann, H. *Tetrahedron Lett.* **1974**, 303. (b) Märkl, G.; Hauptmann, H.; Advena, J. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 441.

(15) The photochemical rearrangement of 7 to the diazirine 26 is not unusual because the photoisomerization of (trimethylsilyl)diazomethane to (trimethylsilyl)diazirine has been found. See ref 5c and 5d.

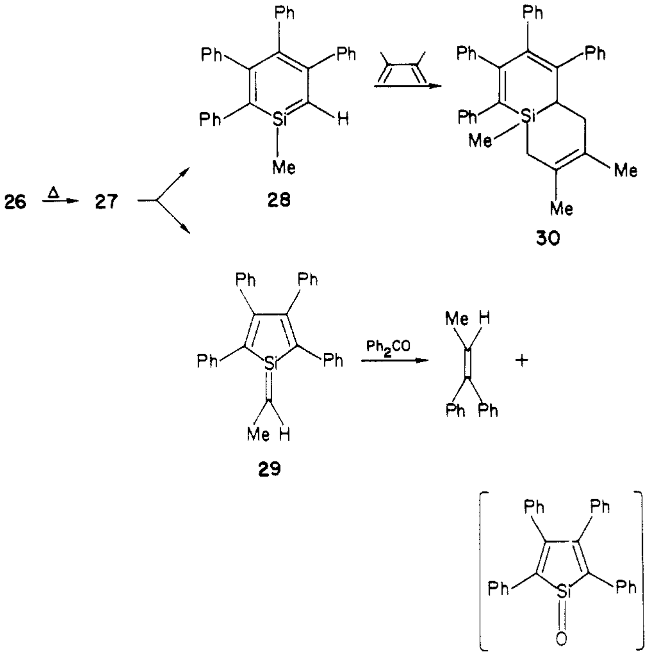
(16) 1,4 addition of methanol to conjugated silenes has precedent; see ref 9g. (a) Ishikawa, M.; Kumada, M. *Adv. Organomet. Chem.* **1981**, *19*, 51. (b) Kyushin, S.; Nakadaira, Y.; Sakurai, H. 47th Annual Meeting of the Chemical Society of Japan, Kyoto, April 1983, Abstr 3B 36.

(17) Sekiguchi, A.; Ando, W. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1675.

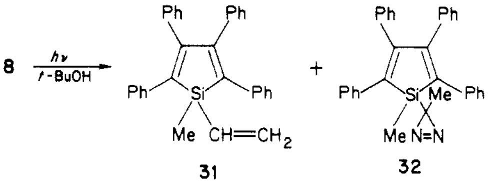
Scheme VI



Scheme VII



Scheme VIII



started after a few minutes, the flask was cooled to 0 °C and additional THF (40 mL) was added. The stirring was continued at 0 °C for 1 h and at room temperature for 2 h. The solution became deep black-purple. To the Grignard reagent was added a solution of diphenylphosphoryl azide, $Ph_2P(O)N_3$ (8.0 g, 29.0 mmol), in THF (10 mL) at 0 °C. The mixture was stirred at 0 °C for 1 h and at room temperature for 24–72 h. The reaction mixture was poured into water and extracted with ether. The ethereal solution was dried over anhydrous sodium sulfate. Evaporation of the ether gave a yellow solid which was filtered to give crude 7. Recrystallization from ether gave pure 7 (7.5 g) in 78% yield as yellow crystals: mp 154–156 °C dec; NMR (CCl_4, δ) 0.58 (s, 3 H, SiMe), 2.88 (s, 1 H, $SiCHN_2$), 6.72–7.28 (m, 20 H, ArH); IR (KBr) 2070 cm^{-1} (N_2); mass spectrum, *m/e* 440 (M^+) and 412 ($M^+ - 28$); UV (hexane) λ_{max} (nm) 243 (ϵ 26800) and 365 (ϵ 7450). Anal. Calcd for $C_{30}H_{24}N_2Si$: C, 81.77; H, 5.49; N, 6.35. Found: C, 81.51; H, 5.66; N, 6.03.

Preparation of (1-Methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)diazirine (26). A solution of 7 (1 g, 2.27 mmol) in benzene (100 mL) was placed in a Pyrex tube and irradiated with a high-pressure mercury lamp through a methanol solution of phenanthrene (10 g/L). The reaction was stopped when the absorption of the diazo group (2070 cm^{-1}) had almost disappeared. Separation of the reaction mixture by silica gel chromatography (eluent carbon tetrachloride) gave **26** (637 mg) in 64% yield as greenish yellow crystals, recrystallized from pentane: mp >78 °C dec; NMR (CCl_4, δ) −0.18 (s, 1 H, CHN_2), 0.37 (s, 3 H, SiMe), 6.76–7.24 (m, 20 H, ArH); ^{13}C NMR ($CDCl_3$) −7.2 (q), 8.8 (d), 126.1 (d), 126.6 (d), 127.5 (d), 128.1 (d), 129.1 (d), 129.8 (d), 136.9 (s), 138.3 (s), 138.7 (s), 156.6 (s) ppm; IR (KBr) 1620 cm^{-1} (N=N); mass spectrum, *m/e* 412 ($M^+ - 28$); UV (hexane) λ_{max} 245 (ϵ 24100) and 366 (ϵ 8690). Anal. Calcd for $C_{30}H_{24}N_2Si$: C, 81.77; H, 5.49; N, 6.35. Found: C, 81.89; H, 5.58; N, 6.13.

Preparation of (1-Methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)diazoethane (8). To a solution of the lithium salt of 7 prepared from LiN-*i*-Pr_2 (LDA) (5.60 mmol) and 7 (1.75 g, 3.97 mmol) was added a solution of methyl iodide (912 mg, 6.42 mmol) in THF (5 mL) at −77 °C. The mixture was stirred at 0 °C for 1 h and at room temperature for 2 h. The reaction mixture was poured into ice water and extracted with ether. The ethereal solution was dried over anhydrous sodium sulfate and concentrated. The residual orange-yellow solid was collected. Recrystallization from pentane/ether gave pure 8 (1.50 g, 83%) as orange-yellow crystals: mp 130–132 °C dec; NMR (CCl_4, δ) 0.61 (s, 3 H, SiMe), 1.26 (s, 3 H, CN_2Me), 6.72–7.25 (m, 20 H, ArH); IR (KBr) 2030 cm^{-1} (N_2); mass spectrum, *m/e* 454 (M^+) and 426 ($M^+ - 28$). Anal. Calcd for $C_{31}H_{26}N_2Si$: C, 81.89; H, 5.76; N, 6.16. Found: C, 81.82; H, 5.76; N, 5.89.

Thermolysis of 4 in *tert*-Butyl Alcohol with Cupric Sulfate. A mixture of 4 (252 mg, 0.556 mmol), *tert*-butyl alcohol (3 mL), benzene (3 mL), and anhydrous cupric sulfate (57 mg) was heated in a sealed tube at 100 °C for 5 min. Separation by silica gel chromatography (eluent benzene) gave 12 (266 mg, 96%) as white crystals: mp 147–148 °C; NMR (CCl_4, δ) −0.23 (s, 6 H, $SiMe_2$), 0.80 (s, 9 H, *t*-Bu), 4.63 (s, 1 H, SiCH), 6.83–7.40 (m, 20 H, ArH); IR (KBr) 1050 cm^{-1} (SiOC); mass spectrum, *m/e* 500 (M^+). Anal. Calcd for $C_{35}H_{36}OSi$: C, 83.94; H, 7.24. Found: C, 83.81; H, 7.25.

Thermolysis of 4 in *tert*-Butyl Alcohol. A mixture of 4 (210 mg, 0.49 mmol), *tert*-butyl alcohol (3 mL), and benzene (3 mL) was heated in a sealed tube at 130 °C for 1 h. Separation by silica gel chromatography gave 12 in 84% yield.

Thermolysis of 4 in Methanol with Cupric Sulfate. A mixture of 4 (248 mg, 0.546 mmol), methanol (3 mL), benzene (3 mL), and anhydrous cupric sulfate (50 mg) was heated in a sealed tube at 100 °C for 10 min. Separation by silica gel chromatography (eluent benzene) gave 14 (184 mg, 91%), recrystallized from benzene/hexane; mp 177–178 °C (lit.[18] mp 177–180 °C).

Thermolysis of 4 in Methanol-d_1 with Cupric Sulfate. A mixture of 4 (202 mg, 0.445 mmol), methanol-d_1 (3 mL), benzene (3 mL), and anhydrous cupric sulfate (53 mg) was heated in a sealed tube at 100 °C for 5 min. Separation by silica gel chromatography (eluent benzene) gave 1,2,3,4-tetraphenyl-5,5-dideuterio-1,3-cyclopentadiene (14) (157 mg, 95%), which was recrystallized from benzene/hexane; mp 177–178 °C. The peak at δ 3.97, attributed to the methylene protons of 1,2,3,4-tetraphenyl-1,3-cyclopentadiene, was absent. Mass spectrum showed the strong parent ion peak at *m/e* 372.

Thermolysis of 12 in Methanol with Cupric Sulfate. A mixture of 12 (170 mg, 0.339 mmol), methanol (3 mL), benzene (1 mL), and anhydrous cupric sulfate (58 mg) was heated in a sealed tube at 100 °C for 10 min. Separation by silica gel chromatography (eluent benzene) gave the desilylated cyclopentadiene 14 (120 mg, 96%).

Thermolysis of 4 in Benzophenone with Cupric Sulfate. A mixture of 4 (151 mg, 0.333 mmol), benzophenone (1.49 g, 8.20 mmol), benzene (2 mL), and anhydrous cupric sulfate (56 mg) was heated in a sealed tube at 100 °C for 10 min. Separation by silica gel chromatography (eluent benzene) gave **15a** (117.8 mg, 66%) as almost black crystals, recrystallized from methanol/benzene; mp 300–302 °C (lit.[19] mp 301–302 °C).

Thermolysis of 4 in Benzophenone. A mixture of 4 (175 mg, 0.39 mmol), benzophenone (1.96 g, 11 mmol), and benzene (6 mL) was heated in a sealed tube at 130 °C for 1 h. Separation by silica gel chromatography gave **15a** in 49% yield.

Thermolysis of 1,2,3,4-Tetraphenyl-1,3-cyclopentadiene 14 in Benzophenone with Cupric Sulfate. A mixture of 14 (40 mg, 0.108 mmol), benzophenone (485 mg, 2.66 mmol), benzene (0.7 mL), and anhydrous cupric sulfate (25 mg) was heated in a sealed tube at 100 °C for 10 min. The cyclopentadiene 14 was recovered, and fulvene **15a** was not detected by TLC.

Thermolysis of 4 in Benzaldehyde with Cupric Sulfate. A mixture of 4 (201 mg, 0.442 mmol), benzaldehyde (3 mL), benzene (1 mL), and anhydrous cupric sulfate (49 mg) was heated in a sealed tube at 100 °C for 5 min. Separation by silica gel chromatography (eluent; benzene) gave **15b** (89 mg, 44%) as rust-red crystals, which were recrystallized from methanol/ethanol, mp 200–201 °C (lit.[19] mp 200–201 °C).

Thermolysis of 5 in Methanol with Cupric Sulfate. A mixture of 5 (520 mg, 1.29 mmol), methanol (5 mL), benzene (4 mL), and anhydrous cupric sulfate (73 mg) was heated in a sealed tube at 100 °C for 4 h. Separation by silica gel chromatography (eluent benzene) followed by HPLC gave 16 (502 mg, 96%): mp 97–98 °C; NMR (CCl_4, δ) 3.27 (s, 3 H, OMe), 4.63 (s, 1 H, SiCHO), 6.87–7.90 (m, 15 H, ArH and BrC=CHSi); mass spectrum, *m/e* 406 (M^+, ^{79}Br) and 408 (M^+, ^{81}Br). Anal. Calcd for $C_{22}H_{19}OSiBr$: C, 64.86; H, 4.70. Found: C, 64.65; H, 4.51.

Photolysis of 5 in Methanol. A solution of 5 (596 mg, 1.48 mmol), methanol (5 mL), and benzene (4 mL) was irradiated through a Pyrex tube with a halogen lamp for 11 h. Separation by TLC gave 16 in 74% yield.

Pyrolysis of 6 with Methanol. Pyrolysis of 6 was performed at ca. 500 °C in a vertical flow pyrolysis apparatus which consisted of a 28 cm × 1 cm Pyrex tube packed with Pyrex chips. The upper end of the tube was equipped with a rubber septum and a nitrogen inlet. A solution of 6 (106 mg, 0.423 mmol), methanol (3 mL), and benzene (0.5 mL) was introduced by syringe through the septum with a stream of nitrogen into the heated Pyrex tube. The pyrolysates were trapped in a receiver cooled by liquid nitrogen. The pyrolysis produced a complex mixture of which the identifiable products were 21 (15%) and 22 (10%). These products were collected by preparative GLC. Product 21 was identified by comparison of its NMR and IR spectra with those of authentic samples. Product 22 was identified by its NMR, IR, and mass spectra and elemental analysis: mp 88–89 °C; NMR (CCl_4, δ) 0.45 (s, 3 H, SiMe), 0.52 (s, 3 H, SiMe), 3.08 (s, 3 H, OMe), 4.88 (s, 1 H, ArCHO), 7.03–7.73 (m, 8 H, ArH); mass spectrum, *m/e* 254 (M^+). Anal. Calcd for $C_{16}H_{18}OSi$: C, 75.53; H, 7.13. Found: C, 75.66; H, 7.14.

Photolysis of 6 in Methanol. A solution of 6 (103 mg, 0.414 mmol), methanol (3 mL), and benzene (0.5 mL) was irradiated through a Pyrex tube with a high-pressure mercury lamp for 10 min. Separation by GLC gave 22 in 95% yield.

Photolysis of 7 in Methanol. A solution of 7 (300 mg, 0.681 mmol), methanol (1 mL), and benzene (5 mL) was irradiated through a Pyrex tube with a high-pressure mercury lamp for 6 h. Separation by HPLC followed by silica gel chromatography (eluent carbon tetrachloride) gave 21 mg of 23 (R = Me, 7%), 24 mg of 24 (R = Me, 8%), 58 mg of 25 (R = Me, 19%), and 134 mg of 26 (48%). The products were identified by the NMR, IR, and mass spectra and elemental analyses.

Compound 23 (R = Me): NMR (CCl_4, δ) 0.06 (s, 3 H, SiMe), 2.33 (s, 2 H, $SiCH_2CPh$), 3.63 (s, 3 H, OMe), 6.74–7.14 (m, 20 H, ArH); IR (KBr) 1085 cm^{-1} (SiOC); mass spectrum, *m/e* 444 (M^+). Anal. Calcd for $C_{31}H_{28}OSi$: C, 83.73; H, 6.34. Found: C, 83.74; H, 6.40.

Compound 24 (R = Me), recrystallized from hexane: colorless crystals; mp 167–168 °C; NMR (CCl_4, δ) 0.56 (s, 3 H, SiMe), 3.32 (s, 3 H, OMe), 5.10 (s, 1 H, =CPhCHPhCPh=), 6.30 (s, 1 H, SiCH=CPh), 6.80–7.29 (m, 20 H, ArH); IR (KBr) 1085 cm^{-1} (SiOC); mass spectrum, *m/e* 444 (M^+). Anal. Calcd for $C_{31}H_{28}OSi$: C, 83.73; H, 6.34. Found: C, 83.76; H, 6.41.

Compound 25 (R = Me), recrystallized from hexane: yellowish green crystals; mp 136.5–137.5 °C; NMR (CCl_4, δ) 0.98–1.05 (m, 5 H, $SiCH_2CH_3$), 3.58 (s, 3 H, OMe), 6.76–7.24 (m, 20 H, ArH); IR (KBr) 1080 cm^{-1} (SiOC); mass spectrum, *m/e* 444 (M^+). Anal. Calcd for $C_{31}H_{28}OSi$: C, 83.73; H, 6.34. Found: C, 83.81; H, 6.37.

Photolysis of 7 in Methanol-d_1. A solution of 7 (300 mg, 0.681 mmol), methanol-d_1 (1 mL), and benzene (5 mL) was irradiated through a Pyrex tube with a high-pressure mercury lamp for 18 h. Separation by HPLC followed by silica gel chromatography gave deuterated products 23 (R = Me, 3%), 24 (R = Me, 27%), 25 (R = Me, 37%), and diazirine 26 (9%).

Compound 23 (R = Me): NMR (CCl_4, δ) 0.02 (s, 3 H, SiMe), 2.28 (s, 1 H, SiCHDCPh), 3.63 (s, 3 H, OMe), 6.72–7.28 (m, 20 H, ArH).

Compound 24 (R = Me): NMR (CCl_4, δ) 0.56 (s, 3 H, SiMe), 3.32 (s, 3 H, OMe), 6.27 (s, 1 H, SiCH=CPh), 6.76–7.40 (m, 20 H, ArH).

Compound 25 (R = Me): NMR (CCl_4, δ) 0.94–1.00 (m, 4 H, $SiCHDCH_3$), 3.56 (s, 3 H, OMe), 6.70–7.22 (m, 20 H, ArH).

Photolysis of 7 in *tert*-Butyl Alcohol. A solution of 7 (300 mg, 0.681 mmol), *tert*-butyl alcohol (1 mL), and benzene (5 mL) was irradiated through a Pyrex tube with a high pressure mercury lamp for 6 h. Separation by HPLC followed by silica gel chromatography (eluent carbon tetrachloride) gave 46 mg of 23 (R = *t*-Bu, 14%), 48 mg of 25 (R = *t*-Bu, 15%), and 107 mg of 26 (38%). The products were identified by their NMR, IR, mass spectra, and elemental analyses.

Compound 23 (R = *t*-Bu), recrystallized from hexane: colorless crystals; mp 149–150 °C; NMR (CCl_4, δ) 0.07 (s, 3 H, SiMe), 1.31 (s, 9 H, *t*-Bu), 2.33 (s, 2 H, $SiCH_2CPh$), 6.70–7.08 (m, 20 H, ArH); IR (KBr) 1050 cm^{-1} (SiOC); mass spectrum, *m/e* 486 (M^+). Anal. Calcd for $C_{34}H_{34}OSi$: C, 83.90; H, 7.04. Found: C, 83.59; H, 7.14. Compound 25 (R = *t*-Bu), recrystallized from hexane: yellowish green crystals; mp 117–118 °C; NMR ($CDCl_3$, δ) 0.98–1.05 (m, 5 H, $SiCH_2CH_3$), 1.24 (s, 9 H, *t*-Bu), 6.75–7.11 (m, 20 H, ArH); ^{13}C NMR ($CDCl_3$) 5.8 (m), 6.0 (m), 31.3 (q), 74.2 (s), 125.7 (d), 126.3 (d), 127.6 (d), 127.8 (d), 129.3 (d), 129.7 (d), 137.2 (s), 139.1 (s), 139.2 (s), 153.9 (s); IR (KBr) 1045 cm^{-1} (SiOC). Anal. Calcd for $C_{34}H_{34}OSi$: C, 83.90; H, 7.04. Found: C, 83.88; H, 7.08.

Photolysis of 7 in Methanol through a Filter Solution. A solution of 7 (238 mg, 0.541 mmol), methanol (1 mL), and benzene (5 mL) was irradiated through a methanol solution of phenanthrene with a high-pressure mercury lamp for 3 h. Separation by HPLC followed by silica gel chromatography gave 18 mg of 23 (R = Me, 8%), 15 mg of 24 (R = Me, 6%), 35 mg of 25 (R =

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(18) Pouchert, C. J.; Campbell, J. R. "The Aldrich Library of NMR Spectra"; Aldrich Chemical Co.; Milwaukee, WI, 1974; Vol. IV, p 34.

(19) Day, J. H. *Chem. Rev.* **1953**, *53*, 167.

Me, 15%), and 139 mg of **26** (54%).

Photolysis of 7 in *tert*-Butyl Alcohol through a Filter Solution. A solution of **7** (300 mg, 0.681 mmol), *tert*-butyl alcohol (1 mL), and benzene (5 mL) was irradiated through a methanol solution of phenanthrene with a high-pressure mercury lamp for 13 h. Separation by HPLC followed by silica gel chromatography gave 33 mg of **23** (R = *t*-Bu, 13%), 33 mg of **25** (R = *t*-Bu, 13%), and 157 mg of **26** (68%).

Photolysis of 26 in *tert*-Butyl Alcohol. A solution of **26** (236 mg, 0.536 mmol), *tert*-butyl alcohol (1 mL), and benzene (5 mL) was irradiated through a Pyrex tube with a high-pressure mercury lamp for 12 h. Separation by HPLC followed by silica gel chromatography gave 33 mg of **23** (R = *t*-Bu, 13%), 49 mg of **25** (R = *t*-Bu, 19%), and recovered **26** (76 mg, 32%).

Thermolysis of 26 in *tert*-Butyl Alcohol. A solution of **26** (321 mg, 0.730 mmol), *tert*-butyl alcohol (2 mL), and benzene (4 mL) was heated in a sealed tube at 150 °C for 10 min. Separation by HPLC followed by silica gel chromatography gave 127 mg of **23** (R = *t*-Bu, 49%) and 81 mg of **25** (R = *t*-Bu, 31%).

Thermolysis of 26 in Methanol. A solution of **26** (235 mg, 0.534 mmol), methanol (2 mL), and benzene (4 mL) was heated in a sealed tube at 150 °C for 10 min. Separation by HPLC followed by silica gel chromatography gave 73 mg of **23** (R = Me, 22%), 70 mg of **24** (R = Me, 22%), and 135 mg of **25** (R = Me, 42%).

Thermolysis of 26 in 2,3-Dimethyl-1,3-butadiene. A solution of **26** (440 mg, 1.00 mmol) in 2,3-dimethyl-1,3-butadiene (5 mL) was heated in a sealed tube at 150 °C for 10 min. Separation by HPLC followed by silica gel chromatography (eluent carbon tetrachloride) gave **30** (70 mg, 14%): NMR (CCl_4, δ) 0.52 (s, 3 H, SiMe), 1.21 (s, 2 H, $SiCH_2C$), 1.64 (s, 3 H, C=CMe), 1.80 (s, 3 H, C=CMe), 2.01 (br t, 1 H, SiCH), 2.92 (br d, 2 H, $SiCCH_2$), 6.85–7.27 (m, 20 H, ArH); ^{13}C NMR ($CDCl_3$) −4.2 (q), 17.0 (t), 21.5 (q), 23.4 (q), 29.2 (d), 37.4 (t), 124.7, 124.9, 125.2, 125.5, 126.2, 126.6, 127.5, 127.6, 127.9, 128.1, 128.3, 128.4, 129.1, 129.8, 130.1 (s), 131.3 (s), 137.5 (s), 138.0 (s), 141.0 (s), 142.0 (s), 142.8 (s), 143.0 (s), 146.2 (s), 150.8 (s); IR (CCl_4) 1250 cm^{-1} (SiMe); mass spectrum, *m/e* 494 (M^+); high-resolution mass calcd for $C_{36}H_{34}Si$ 494.2427, found 494.2424.

Thermolysis of 26 in Benzophenone. A mixture of **26** (250 mg, 0.568 mmol) and benzophenone (750 mg, 4.12 mmol) was heated in a sealed tube at 150 °C for 10 min. Separation by HPLC followed by silica gel chromatography (eluent benzene) gave 1,1-diphenylpropene (15 mg, 14%) which was identified by comparison of its NMR and IR spectra with those of an authentic sample.

Photolysis of 8 in *tert*-Butyl Alcohol. A solution of **8** (300 mg, 0.660 mmol), *tert*-butyl alcohol (2 mL), and benzene (8 mL) was irradiated through a Pyrex tube with a high-pressure mercury lamp for 7 h. Separation by HPLC gave 156 mg of **31** (52%) and 75 mg of diazirine **32** (27%). Products **31** and **32** were identified by their NMR, IR, mass spectra, and elemental analyses.

Compound **31**, recrystallized from hexane: yellowish green crystals; mp 170–170.5 °C (lit.[20] mp 177–178 °C); NMR (CCl_4, δ) 0.58 (s, 3 H, SiMe), 5.76–6.60 (m, 3 H, $SiCH{=}CH_2$), 6.81–7.30 (m, 20 H, ArH); IR (KBr) 1250 cm^{-1} (SiMe); mass spectrum, *m/e* 426 (M^+). Anal. Calcd for $C_{31}H_{26}Si$: C, 87.27; H, 6.14. Found: C, 87.17; H, 6.14.

Compound **32**, recrystallized from pentane: yellowish green crystals; mp 142 °C dec; NMR (CCl_4, δ) 0.21 (s, 3 H, SiMe), 0.91 (s, 3 H, CN_2Me), 6.76–7.36 (m, 20 H, ArH); IR (KBr) 1610 cm^{-1} (N=N); mass spectrum, *m/e* 426 ($M^+ - 28$); ^{13}C NMR ($CDCl_3$) 7.5 (q), 15.6 (s), 18.4 (q), 125.6 (d), 126.1 (d), 126.3 (d), 126.6 (d), 127.6 (d), 127.9 (d), 128.2 (d), 129.1 (d), 129.8 (d), 130.0 (d), 137.3 (s), 138.4 (s), 138.7 (s), 156.6 (s) ppm. Anal. Calcd for $C_{31}H_{26}N_2Si$: C, 81.89; H, 5.76; N, 6.16. Found: C, 82.08; H, 5.80; N, 5.95.

Acknowledgment. We are grateful to the Shinetsu Chemical Co. for partial support of this work. This research is supported by Grant-in-Aid for Scientific Research (No. 59740240).

Registry No. **4**, 77999-12-3; **5**, 77999-16-7; **6**, 82644-70-0; **7**, 89175-80-4; **7** (lithium salt), 94671-27-9; **8**, 94671-28-0; **12**, 77999-13-4; **14**, 15570-45-3; **14**-d_2, 77999-14-5; **15a**, 77999-15-6; **15b**, 6937-59-3; **16**, 77999-17-8; **21**, 21993-93-1; **22**, 94671-29-1; **23** (R = Me), 89175-85-9; **23** (R = *t*-Bu), 89175-82-6; **23**-d_1 (R = Me), 94671-30-4; **24** (R = Me), 89175-83-7; **24**-d_1 (R = Me), 94671-31-5; **25** (R = Me), 89175-86-0; **25** (R = *t*-Bu), 89175-84-8; **25**-d_1 (R = Me), 94671-32-6; **26**, 89175-81-5; **30**, 89175-87-1; **31**, 51528-39-3; **32**, 94671-33-7; $Ph_2P(O)N_3$, 26386-88-9; 1-methyl-1-(chloromethyl)-2,3,4,5-tetraphenyl-1-silacyclopentadiene, 94671-34-8; 1,1-diphenylpropene, 778-66-5; 2,3-dimethyl-1,3-butadiene, 513-81-5.

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Carbon Monoxide Activation by Iridium(III) Dicationic Carbonyl Complexes

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Received June 8, 1984

The cationic *cis*- and *trans*-$IrX(CO)(dppe)_2{}^{2+}$ (X = H, Cl) species react with nucleophiles, such as H_2O, OH^-, and H^-, to afford hydroxycarbonyl and formyl cations of Ir(III) typified by the species *trans*-$IrH(COOH)(dppe)_2{}^+$ and *trans*-$IrX(CHO)(dppe)_2{}^+$. The formyl complexes are protonated by strong acids to afford the electrophilic dicationic hydroxycarbene complexes *trans*-$IrX(CHOH)(dppe)_2{}^{2+}$. Reactivities and stabilities of these species are discussed.

Introduction

The reactions of coordinated carbon monoxide have long been a topic of interest because of the involvement of carbon monoxide in a variety of organotransition-metal-catalyzed reactions in which useful organic molecules are synthesized.[1,2] Catalysis of carbon monoxide hydrogenation[3] and the water gas shift reaction[4-10] are two areas that have received considerable attention. Modeling of species thought to be intermediates in these processes[11-13] has been

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